DETERMINATION OF NITRATE-NITROGEN IN WATER USING A COATED WIRE ELECTRODE

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INTRODUCTION

Monitoring nitrate (NO_3) in water has important implications to public health and environmental quality. Of the analytical methods available, ion selective electrodes have potential for simple, rapid determination of NO_3 concentrations in water. Use of ion selective electrodes has been limited due to interference by a variety of ions, relatively high detection limits, and short operational lifetimes (Tabatabi and Dick, 1983). According to Langmuir and Jacobson (1970) chloride (Cl) and bicarbonate (HCO_3) were the chief interfering anions in most waters when using a commercially available liquid junction NO_3 specific electrode. Lee et al (1986) described a procedure for making coated wire nitrate-selective electrodes. In this paper, we report the characteristics of the coated wire NO_3 selective electrode and the possible application to NO_3 analysis in water.

MATERIALS AND METHODS

Coated wire NO_3 selective electrodes were prepared using Aliquat 336S as the ion exchanger according to the technique of Lee et al (1986). The detection limits of the electrode, interferences from chloride (Cl) as potassium chloride, nitrite (NO_2) as sodium nitrate, bicarbonate (HCO_3) as sodium bicarbonate, sulfate (SO_4) as sodium sulfate, acetate as sodium acetate, and orthophosphate (H_2PO_4) as sodium phosphate (NaH_2PO_4) and the operational pH range were determined using freshly prepared standard solutions. Electrode potentials were determined using a Model 601 Orion pH/ion meter and a Fisher model 13-639-53 Ag/AgCl reference electrode.

Water samples were collected from a stream-fed lake in Spalding County, Georgia, and wells in Henry and Lamar counties in Georgia. A precipitation sample was collected on September 7, 1987, using a polyethylene funnel and bottle. Fog was collected on September 23, 1987, using a fog water collector described by Falconer and Falconer (1980).

Nitrate, chloride and sulfate were determined by single column ion chromatography using a Wescan model 213A conductivity detector, a VYDAC 302 I.C. column and a Beckman 110A pump. The solvent (0.004 M potassium hydrogen phthalate, pH 4.5) flow rate was 2 ml/min. All samples were analyzed in triplicate.

RESULTS AND DISCUSSION

The potential of an ion selective electrode, measured in millivolts, is related to ion activity according to the Nernst equation:

$$E = E^o + \frac{2303RT}{zF} \text{ Log } (a) \quad \text{where} \qquad (1)$$

E is the experimentally observed potential of the ion-selective electrode,
R is the gas constant (8.31441 JK^{-1} mol^{-1}),
T is the thermodynamic temperature (^oK),
F is the Faraday constant (9.6485 x 10^4C mol),
a is the activity of the ion (in moles 1^{-1}),
z is an integer with sign and magnitude corresponding to the charge of the ion,
E^o is a constant including the standard potential of the indicator electrode, the reference electrode potential, and the junction potential.

The NO_3 selective electrode response to increasing NO_3-N concentrations from 10^{-5} to 10^{-2}M in distilled water (check) and in 10^{-3}M solutions of various anions is shown in Fig. 1. The average response from 10^{-5} to 10^{-2}M NO_3-N in distilled water was 60 mV per decade change in concentration compared to 59 mV predicted by the Nernst equation at 25°C. The electrode response is decreased considerably in 10^{-3}M solutions of NO_2-N, Cl and HCO_3 (Fig. 1). In 10^{-3}M sodium acetate the electrode follows the theoretical response in the range from 10^{-4} to 10^{-2}M NO_3-N. The interference of H_2PO_4 and SO_4 appeared to be insignificant in the range from 10^{-5} to 10^{-2}M NO_3-N. The addition of 10^{-3}M Ag_2SO_4 improved the electrode response to NO_3 in 10^{-3}M Cl (Fig. 1). This was presumably due to the pre

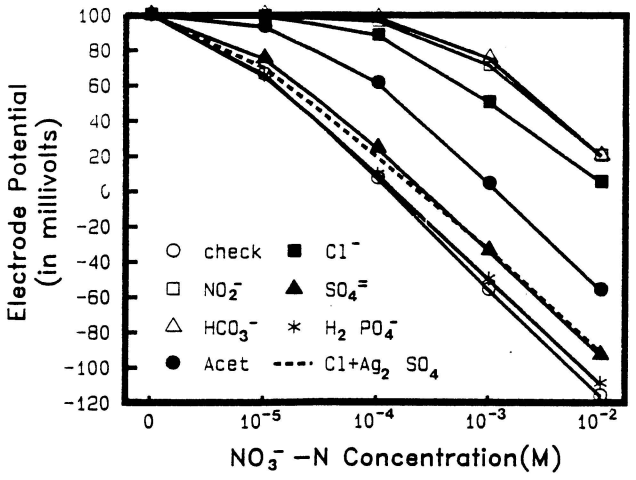

Figure 1. Effect of Various Anions at 10^{-3} M on NO3 Selective Electrode Response

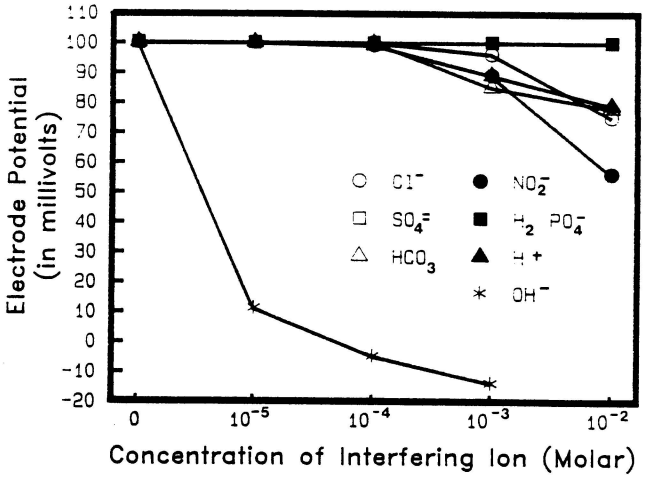

Figure 2. Effect of the Addition of Various Ions on NO3 Selective Electrode Response in 10^{-3} M NO3-N

cipitation of AgCl from the solution. We speculate that the ion exchanger in the electrode is more selective for monovalent anions than for divalent or trivalent anions. As a result monovalent anions (e.g. Cl, NO_2, HCO3 and acetate) are more likely to affect the sensitivity of the NO3 selective electrode.

The response of the NO3 selective electrode to addition of various anions in 10^{-3}M NO3-N is presented in Fig. 2. Hydroxide ion (OH) affected the electrode at 10^{-5}M (pH = 9), and at 10^{-2}M OH (pH = 12) the electrode displayed irreversible failure. The monovalent anions (NO_2, HCO3, and Cl) began to affect the electrode response at 10^{-3}M concentrations with increasing effect at 10^{-2}M in the order NO_2 > Cl = HCO3. The electrode did not respond to SO4 and H_2PO_4 concentrations up to 10^{-2}M in 10^{-3}M NO3-N solutions (Fig. 2). The pH range in which the electrode operates without interference was from 4 to 9. The electrode responded to 10^{-3}M H and the effect was greater in 10^{-2}M H (Fig. 2).

Comparison of NO3 analysis of water using the NO3 selective electrode and ion chromatography are presented in Table 1. The electrode gave consistently higher values for NO3 concentrations than the ion chromatograph. In the case of the lake water sample, no NO3 was detected by the ion chromatograph compared to 0.045 x 10^{-3}M using the NO3 selective electrode (Table 1). We speculate that the detection limit for the electrode is lower than for the ion chromatograph resulting in greater sensitivity at lower NO3 concentrations for the electrode.

Where interfering ions are present, equation (1) can be expanded to include terms for the activity of the interfering ion (Langmuir and Jacobson, 1970). The Cl concentrations in these water samples are below the levels which would interfere with NO3 determination using the electrode (Fig. 2). The pH range of the samples is also within the operating range of the electrode (Table 1).

Based on our observations, the coated wire NO3 selective electrode has an operational lifetime greater than 6 months. The electrode drift was minimal, and the equilibration time between samples was usually less than 1 min. The results of this study indicate that this type of NO3 selective electrode was capable of rapid, accurate determinations of NO3-N concentrations in natural water when concentrations of interfering ions are sufficiently low.

CONCLUSIONS

Ion selective electrodes have potential for simple, rapid determination of nitrate (NO3) concentrations in water. Operating characteristics and interferences were determined for a recently developed solid state NO3 selective electrode. Also, several water samples were analyzed for nitrate (NO3) using the solid state NO3 selective electrode and single column ion chromatography. The electrode operated in a pH range from 4 to 9. Monovalent anions (nitrite, bicarbonate and chlo-

Table 1. Comparison of NO_3^- Determinations in Water Between a NO_3^- Selective Electrode and an Ion Chromatograph.

	Electrode	Ion chromatograph			
	NO_3^- -N	NO_3^- -N	Cl^-	$SO_4^=$ -S	pH
	concentration (10^{-3}M)				
Fog (9-23-87)	0.94(0.02)†	0.67(0.02)	0.22(0.004)	0.085(0.0003)	6.34
Rainwater (9-7-87)	1.20(0.02)	1.1 (0.06)	0.10(0.002)	0.21(0.002)	4.77
Lake water (Spalding County)	0.045(0.002)	N.D.‡	0.044(0.001)	0.016(0.0002)	7.28
Well water					
(Lamar County)	0.37 (0.02)	0.31 (0.02)	0.23 (0.002)	N.D.	6.00
(Henry County)	0.088(0.002)	0.058(0.001)	0.048(0.002)	N.D.	6.09

†Sample standard deviation

‡Sample concentration was below detection limits of the ion chromatograph

ride) affected the electrode response at concentrations of 10^{-3} M and higher. The electrode was not affected by sulfate and orthophosphate concentrations up to 10^{-2} M. Nitrate concentrations in the water samples ranged from 0.045 to 1.2 x 10^{-3} M using the NO3 selective electrode compared to concentrations ranging from below the detection limit to 1.1 x 10^{-3} M for the same samples analyzed with the ion chromatograph. The water samples used in this study did not appear to have high enough concentrations of interfering species to affect the operation of the electrode. The higher NO3 concentrations reported using the electrode compared to the ion chromatograph were attributed to the higher sensitivity of the electrode.

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